High-Performance of SATS-Derived $CaO/TiO_2–Al_2O_3$ Sorbent for CO_2 Capture in Batch Fluidized Bed

Weiwei Peng, Zuwei Xu, and Haibo Zhao

Abstract

CaO-based sorbents are widely used to capture CO_2 in calcium looping (Ca-L) and chemical looping gasification (CLG) processes due to its relatively low material cost, high availability, fast kinetics and high theoretical CO_2 capture capacity. However, a major challenge for Ca-L technology is the rapid decay of CaO during successive carbonation/calcination cycles. To overcome this loss-in-capacity defect, a novel self-assembly template synthesis (SATS) method is proposed to manufacture a hierarchical structure CaO-based sorbent ($CaO/TiO_2–Al_2O_3$ sorbent). In this study, CaO sorbent (made by calcination method), CaO/Al_2O_3 sorbent (made by impregnation method), and $CaO/TiO_2–Al_2O_3$ sorbent (made by SATS method) are manufactured to evaluate their performance on a laboratory scale. The carbonation/calcination cyclic tests of CaO-based sorbents are conducted in batch fluidized bed; in addition, the morphology features and mechanical strength before and after cyclic tests are also researched. After 10 successive cycles, it can be found that $CaO/TiO_2–Al_2O_3$ sorbent achieves high CO_2 capture capacity of 0.78 mol CO_2/mol CaO, which is 46 and 36 % higher than those of CaO and CaO/Al_2O_3, respectively. Meanwhile, $CaO/TiO_2–Al_2O_3$ sorbent shows high mechanical strength with an appreciable crushing strength of 1.46 N and high sintering resistance with a rich and uniform porous structure. Therefore, it can be concluded that $CaO/TiO_2–Al_2O_3$ sorbent performs high and durable capture capacity, stable thermal stability, strong mechanical strength and sintering resistance compared with CaO and CaO/Al_2O_3 sorbents in batch fluidized bed.

Keywords

Cao-based CO_2 sorbent • SATS method • Batch fluidized bed • Mechanical strength

W. Peng · Z. Xu · H. Zhao (✉)
State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, 1037 Luoyu Road, Wuhan, 430074, China
e-mail: klinsmannzhb@163.comhzhao@mail.hust.edu.cn

W. Peng · H. Zhao
China-EU Institute for Clean and Renewable Energy, Huazhong University of Science and Technology, 1037 Luoyu Road, Wuhan, 430074, China

G. Yue and S. Li (eds.), *Clean Coal Technology and Sustainable Development*,
DOI 10.1007/978-981-10-2023-0_45

1 Introduction

Anthropogenic emission of CO_2 from the combustion of fossil fuels is the main contributor to global warming and climate changes. Developing post-combustion CO_2 capture technologies is believed as one of the most promising technologies to alleviate CO_2 emission [1].

Calcium looping (Ca-L) technology, which aims at reducing CO_2 capture costs and energy penalties associated with the separation of CO_2, is believed as an effective post-combustion method [2–4]. The Ca-L technology takes advantage of the following reversible carbonation of CaO:

$$CaO + CO_2 = CaCO_3 \quad \Delta H_r^0 = -179\,\mathrm{kJ/mol} \qquad (1)$$

However, the major challenge in developing Ca-L technology is the problem of loss in capacity, the main reason for this can be identified in severe sintering at high temperature during calcination process, leading to a reduction in available surface area for reaction [5, 6]. In addition, commercial CaO-based sorbents have sub-optimal mechanical properties causing high attrition rates and, consequently, elutriation of fine materials when used in fluidized bed reactor systems [7–9]. Synthesizing CaO-based composite materials is regarded as one of most efficient methods because it is helpful for suppressing sorbent sintering, attrition, and agglomeration according to some literatures [10–12].

A large number of cyclic tests of synthetic sorbents were reported, but most of previous works were conducted in a TGA reactor, where was not exposed to attrition, as in a fluidized bed. Moreover, some results of cyclic tests in fluidized beds were not satisfactory as expected, which were mainly reflected in undesired CO_2 capture capacity and poor physical strength. Fennell et al. [13] studied the attrition rate of the particles of five limestones in a fluidized bed, and it was found that most limestones lost approximately 10 % of their mass over the course of a typical experiment; moreover, the carbonation conversion of limestone dropped to a very low level after a few cycles, which only retained 20–30 % of initial CO_2 capture capacity. Coppola et al. [14] compared the performance of six European limestones during Ca-L cycles both in a laboratory-scale fluidized bed and in a thermo-gravimetric apparatus, and results showed that the CO_2 capture capacity of the sorbents measured in TGA tests was generally larger than that measured in fluidized bed reactor.

In this work, $CaO/TiO_2–Al_2O_3$ sorbent was manufactured by the SATS method and then tested in a laboratory batch-operated fluidized bed reactor. In addition, physical characterizations of morphology features and mechanical strength were also assessed. All of tests referred above were also experimented for CaO and CaO/Al_2O_3 to evaluate their performance on a laboratory-scale basis so that those with the best CO_2 capture performance were selected for further larger-scale testing.

2 Experimental

2.1 Materials

In this study, calcium acetate monohydrate power (Sinopharm chemical reagent Co. Ltd., Shanghai, China), commercial Al_2O_3 powder (Sinopharm chemical reagent Co. Ltd., Shanghai, China), and flame-synthesized TiO_2 nanoparticles made in our laboratory were chosen as raw materials.

2.2 Preparation of Sorbents

Pure CaO and CaO/Al_2O_3 (80 wt%:20 wt%) were manufactured by calcination method and wet impregnation method, respectively. $CaO/TiO_2–Al_2O_3$ (80 wt%:5 wt %:15 wt%) was obtained by a novel self-assembly template synthesis (SATS) method. The detail experiment procedures were introduced in our previous work.

2.3 Cyclic Carbonation/Calcination Test in Fluidized Bed

2.3.1 Minimum Fluidization Velocity in Theory

Prior to the start of each experiment, CaO-based particle was sieved to ensure that all particles were initially between 200 and 300 μm in size with a weight of 2.5 g for each sorbent. The results of physical property parameters of CaO-based sorbents are listed in Table 1, where ρ_f, μ_f, μ_{mf}, and L presented density of fluidization gas, dynamic viscosity of gas flow, minimum fluidization velocity, and inlet gas flow, respectively. Gas flow of 800 ml/min was chosen as

Table 1 Physical property parameters of CaO-based sorbents under different temperature

	CaO			CaO/Al_2O_3		$CaO/TiO_2–Al_2O_3$	
	700 °C		900 °C	700 °C	900 °C	700 °C	900 °C
	10 %CO_2	N_2		10 %CO_2	N_2	10 %CO_2	N_2
ρ_f (kg/m^3)	0.37	0.29		0.37	0.29	0.37	0.29
μ_f (kg/m/s)	40.70	46.10		40.70	46.10	40.70	46.10
μ_{mf} (m/s)	0.02	0.02		0.02	0.03	0.03	0.02
L (mL/min)	219.30	160.90		240.20	176.30	268.10	215.10

superficial gas velocity in our study to satisfy bubbling fluidization with three to five times of minimum fluidization velocity.

2.3.2 Cyclic Carbonation/Calcination Process in Fluidized Bed

A laboratory batch fluidized bed reactor was used to investigate the reaction performance and the multi-cycling stability of CaO-based sorbents. As illustrated in Fig. 1, the reactor mainly consists of the gas control unit, the reaction unit, and the gas detection unit.

The gas control unit provided 10 vol.% CO_2 (balanced with N_2) or pure N_2 as the fluidization gas. The fluidization gas was introduced into the fluidized bed from the bottom of reactor. The reaction unit included a stainless reaction tube with a length of 892 mm placed into an electrical furnace. A porous plate with a diameter of 26 mm was set in the tube at 400 mm from the bottom. The reactor temperature was measured by a type K thermocouple at about 10 mm above the porous plate. CaO-based sorbents were introduced through the hopper on the top of the reactor before cyclic test. All gaseous products exiting the reactor were first led to filter to remove fine particles, and then to an electric cooler to remove the steam, and finally to a gas analyzer, i.e., the gas detection unit, to determine the concentration of CO_2, which was further recorded by a computer every second.

Carbonation/calcination experiments were carried out batchwise for the each of CaO-based particles, i.e., no adding particles during the run; 2.5 g of CaO-based particles were first exposed to N_2 atmosphere for 30 min at the set-point temperature of 900 °C to ensure initial complete calcination. Then, the temperature was down to 700 °C for carbonation process with 10 vol.% CO_2 (balanced with N_2) flow for 30 min. Next, the fluidization gas was switched rapidly from 10 vol.% CO_2 to N_2, and then the temperature was up to 900 °C for calcination process for 5 min. Then, the temperature was down to 700 °C again for the next carbonation/calcination cycle; 10 carbonation/calcination cycles were conducted for three CaO-based sorbents. It is noted that the CO_2 capture capacity was calculated on the basis of the amount of CO_2 absorbed during the conversion from CaO to $CaCO_3$ of the carbonation process.

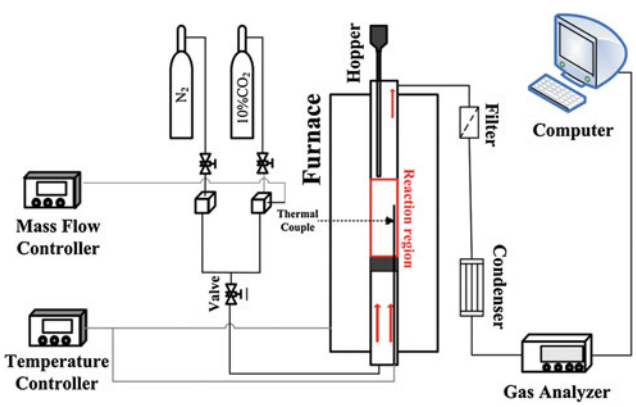

Fig. 1 A diagrammatic sketch of the fluidized bed reaction system

2.4 Physical Measurements

The crushing strength determined using a digital dynamometer (Shimpo, FGJ-5) was taken as the average value of 40 measurements of the force needed to crush a sorbent particle. The microstructure of sorbents was investigated by environmental scanning electron microscope (Quanta 200, FEI) with 20 kV of accelerating voltage.

3 Results and Discussion

3.1 CO_2 Capture Performance in Batch Fluidized Bed

The evolution of CO_2 capture capacity of three CaO-based sorbents was shown in Fig. 2. It was found that CaO/TiO_2–Al_2O_3 sorbent, which was manufactured by the SATS method, exhibited maximum initial CO_2 capture capacity of 0.78 mol CO_2/mol CaO (mol/mol for logogram in following descriptions), compared with 0.62 mol/mol and 0.57 mol/mol for CaO/Al_2O_3 and CaO, respectively. The relative poor CO_2 capture capacity of CaO and CaO/Al_2O_3 at first cycle may be ascribed to pre-calcination process, which resulted in sintering of active CaO material and reduction in pore plugging. Then, a loss-in-capacity

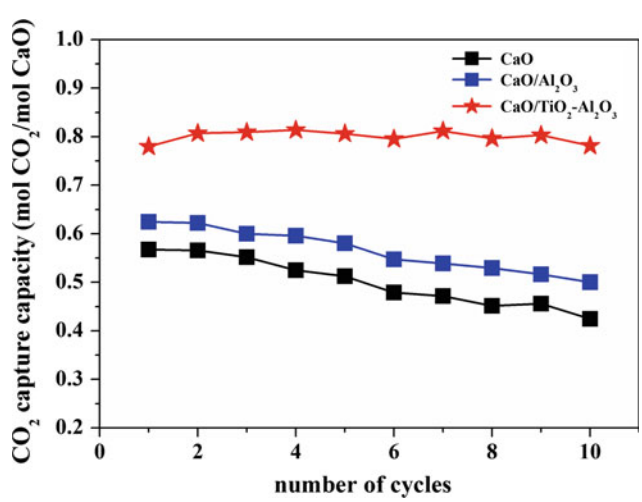

Fig. 2 Evolution of CO_2 capture capacity for CaO, CaO/Al_2O_3 and CaO/TiO_2–Al_2O_3 during 10 cycles in batch fluidized bed, carbonated at 700 °C in 10 vol.% CO_2 for 30 min and calcined at 900 °C in pure N_2 for 5 min

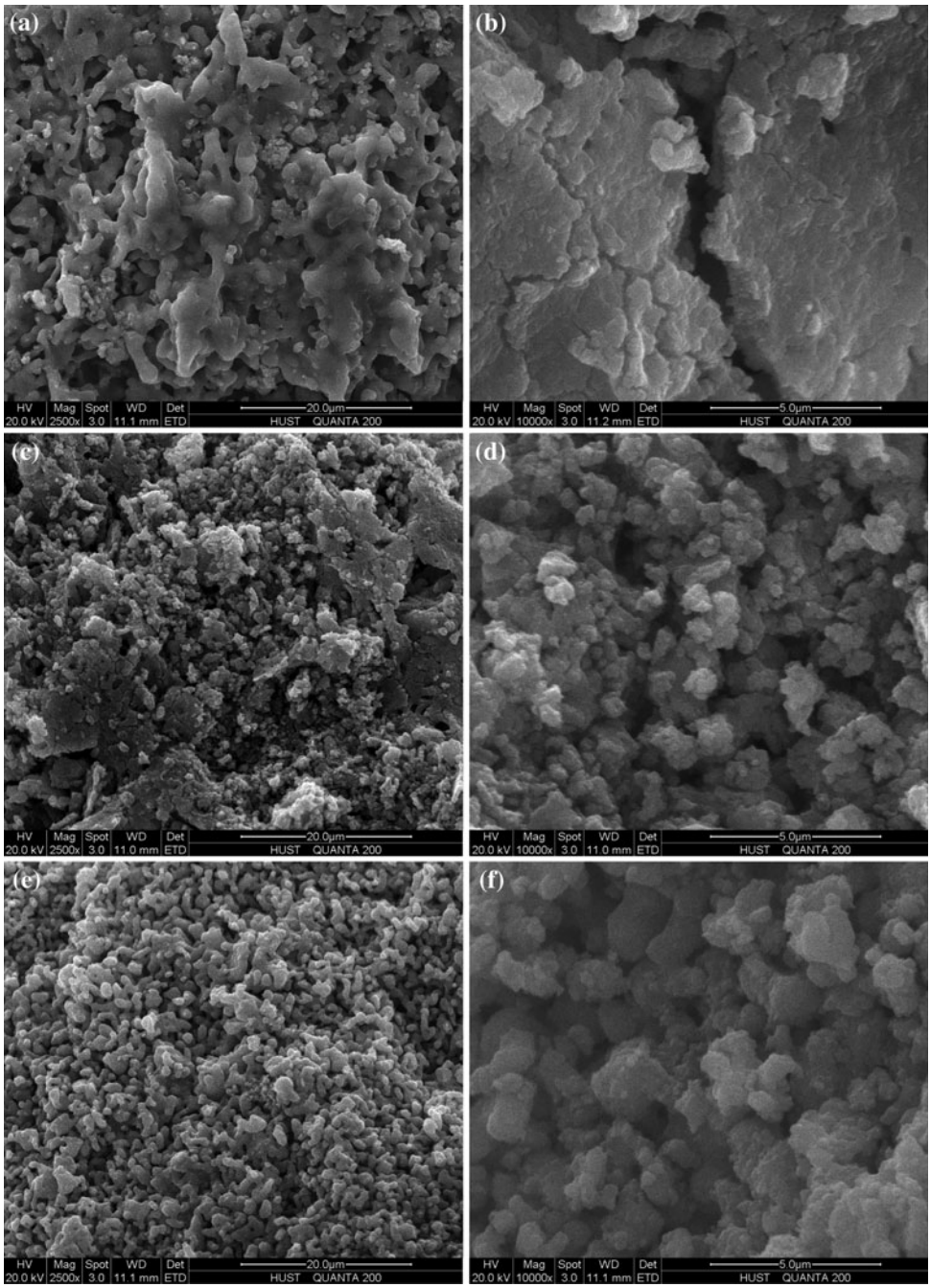

Fig. 3 ESEM images of sorbents: the *left row* shows used sorbents with the magnifying power of 2500 (**a**, **c**, **e**); the *right row* shows used sorbents after 10 cycles with the magnifying power of 10000 (**b**, **d**, **f**); the *upper column* presents CaO (**a**, **b**); the *middle column* presents CaO/Al_2O_3 (**b**, **d**); the *lower column* presents CaO/TiO_2–Al_2O_3 (**e**, **f**)

phenomenon of CaO and CaO/Al_2O_3 sorbent was exposed during successive cycles.

As for CaO/TiO_2–Al_2O_3 sorbent experienced 10 cycles in fluidized bed, it maintained a surprising CO_2 capture capacity of 0.78 mol/mol, which was 46 and 36 % higher than those of CaO and CaO/Al_2O_3 respectively. The CO_2 capture capacity of CaO/TiO_2–Al_2O_3 remained almost 100 % of the initial CO_2 capture amount, presenting superior performance in terms of both capture capacity and stability. The reason for high-capacity property and long-term stability of CaO/TiO_2–Al_2O_3 sorbent may be attributed to the formation of core-shell (Al_2O_3–TiO_2) structure, which inhibited the chemical reaction between active CaO phase and Al-based materials; in addition, the high melting ability of sorbent was helpful to its sintering resistance and the high mechanical strength was benefit for cyclic stability during multiple cycles.

3.2 Physical Measurements

It is well known that the textural change in CaO-based sorbents, such as grain growth and pore closure, caused by serious sintering during the cyclic process, contributed to the deactivation of the CaO-based sorbents in the Ca-L cycles. To have a comprehensive understanding of three CaO-based sorbents, the morphological images of sorbents after 10 cyclic tests in fluidized bed were achieved by environmental scanning electron microscope (ESEM) and are presented in Fig. 3.

In our previous study, it was reported that fresh CaO-based sorbents had developed porous structure, which provided a larger surface area for CO_2 capture; however, it can be found that a significant change in the samples in porosity and morphology appeared after multiply cycles when tested in TGA reactor. As shown in Fig. 3, a similar ESEM result of CaO-based sorbents in fluidized bed was found. As can be seen in Fig. 3a, CaO sorbent lost coarse surface and porous morphology after 10 cycles, demonstrating that CaO sorbent suffered from a serious sintering in fluidized bed, which also was confirmed by clear crack and aggregation phenomenon appeared in Fig. 3b. It can be seen that adding all of the support materials (Al_2O_3 or $TiO_2–Al_2O_3$) played a key role in suppressing sintering of synthetic sorbent to a certain degree, but there were considerable differences in the improvements. As for CaO/Al_2O_3, a less serious sintering phenomenon of particles, increased particle density and part pore blocking appeared. Morphology characterization of CaO/Al_2O_3 remained a reasonable acceptance, which benefited from high melting and strong mechanical strength as a result of adding Al-based support. In contrast, $CaO/TiO_2–Al_2O_3$ sorbent maintained a rich and quiet uniform porous structure, and the interconnected pore distribution and unique core-shell structure ensured high reactivity, satisfactory mechanical properties and sintering resistance, which contributed to prominent CO_2 capture capacity during multiply carbonation/calcination cycles in batch fluidized bed.

It was reported that the commercialization of Ca-L faced two severe technical problems of the CaO-based sorbents. One was a well-known problem of loss in capacity as a result of a sintering-induced textural structure change when subjected to repeated cycles, which was confirmed by our study introduced above. The other was the mechanical resistance, which has been reported to be a significant problem, because the poor mechanical resistance performance induced mass loss from the reactor and caused a marked increase in the sorbents' makeup. Therefore, all of three CaO-based sorbents in our study need to be assessed of their mechanical resistance.

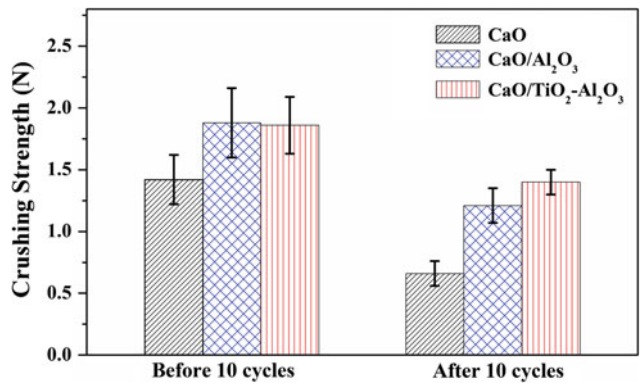

Fig. 4 Crushing strength results for CaO, CaO/Al_2O_3, $CaO/TiO_2–Al_2O_3$ before and after 10 cyclic tests in batch fluidized bed, carbonated at 700 °C in 10 vol.% CO_2 for 30 min and calcined at 900 °C in pure N_2 for 5 min

Crushing strength can be used as a fast screening method for evaluating the mechanical resistance of CaO-based sorbents [15]. The crushing strength of each sorbent with a particle size range from 200 to 300 μm was taken as the average value of 40 measurements of the force needed to crush CaO-based particle. The results in Fig. 4 showed that the crushing strength of three CaO-based sorbents was reduced with the increase of cyclic numbers, and the standard deviation of the measurement also decreased. In detail, the crushing strengths of fresh CaO, CaO/Al_2O_3, and $CaO/TiO_2–Al_2O_3$ were 1.46, 1.88, and 1.86 N, respectively, compared with 0.66 N, 1.21 N, 1.46 N for used CaO, CaO/Al_2O_3, and $CaO/TiO_2–Al_2O_3$. The effects of support material adding, including Al_2O_3 and $TiO_2–Al_2O_3$, on the enhancement of the crushing strength of sorbents were revealed here. More specifically, $CaO/TiO_2–Al_2O_3$ sorbent had the highest crushing strength and kept a high mechanical stability, which were helpful for attrition resistance. However, the mechanical strength of CaO-based sorbent referred in this study should be significantly improved to satisfy the industrial demand when comparing with other solid particles such as oxygen carriers.

4 Conclusion

A comprehensive study has been undertaken to investigate and explore the cyclic performance of CaO (made by calcination method), CaO/Al_2O_3 (made by wet impregnation method), and $CaO/TiO_2–Al_2O_3$ (made by Self-Assembly Template Synthesis method) in batch fluidized bed. The SATS-derived $CaO/TiO_2–Al_2O_3$ sorbent possessed a high-capacity and long-life performance of 0.78 mol/mol after 10 carbonation/calcination cycles in batch fluidized

bed, which is 46 % and 36 % higher than those of CaO and CaO/Al_2O_3, respectively. The results of ESEM proved its sintering-resistance textural structure and confirmed the advantage of SATS-derived sorbent. In addition, crushing strength tests proved that $CaO/TiO_2–Al_2O_3$ sorbent presented high mechanical strength and favorable long-life property.

Acknowledgment This work was funded by the National Natural Science Foundation of China (Grant No. 51390494 and 51276077). The authors are grateful to the Analytical and Testing Center of HUST for ESEM measurements.

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